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# Subnanometer three-dimensional atom-probe investigation of segregation at MgO/Cu ceramic/metal heterophase interfaces

J.T. Sebastian<sup>a,\*</sup>, J. Rüsing<sup>a</sup>, O.C. Hellman<sup>a</sup>, D.N. Seidman<sup>a</sup>, W. Vriesendorp<sup>b</sup>,  
B.J. Kooi<sup>b</sup>, J.Th.M. De Hosson<sup>b</sup>

<sup>a</sup> *Department of Material Science and Engineering, Northwestern University, Evanston, IL, USA*

<sup>b</sup> *Department of Applied Physics, University of Groningen, Groningen, Netherlands*

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## Abstract

Three-dimensional atom-probe (3DAP) microscopy has been applied to the study of segregation at ceramic/metal (C/M) interfaces. In this article, results on the MgO/Cu(X) (where X = Ag or Sb) systems are summarized. Nanometer-size MgO precipitates with atomically clean and atomically sharp interfaces were prepared in these systems by internal oxidation. Segregation of the ternary component (Ag or Sb) at the MgO/Cu heterophase interface was enhanced by extended low-temperature anneals. Magnesia precipitates in the 3DAP reconstructions were delineated as isoconcentration surfaces, and segregation of each ternary component at the C/M interfaces was analyzed with the proximity histogram method developed at Northwestern University. This method allows the direct extraction of the Gibbsian interfacial excess of solute at the C/M interfaces from the experimental data. A value of  $(3.2 \pm 2.0) \times 10^{17} \text{ m}^{-2}$  at 500°C is obtained for the segregation of Ag at a MgO/Cu(Ag) interface, while a value of  $(2.9 \pm 0.9) \times 10^{18} \text{ m}^{-2}$  at 500°C is obtained for the segregation of Sb at a MgO/Cu(Sb) interface. The larger Gibbsian excess for Sb segregation at this ceramic/metal heterophase interface is most likely due to the so-called  $p\Delta V$  effect. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Three-dimensional atom-probe microscopy; Ceramic/metal; MgO/Cu; Segregation; Heterophase interfaces

## 1. Introduction

Ceramic/metal (C/M) interfaces are pervasive in materials science and engineering. They play a critical role in a large number of important technological applications, including metal-matrix composites, supported catalysts, electronic packa-

ging, and thermal barrier coatings on nickel- or iron-based superalloys employed at elevated temperatures. The scientific study of C/M interfaces, however, is in a nascent stage, and atomic-resolution techniques have only recently been utilized to explore experimentally their structure, chemistry, and electronic properties.

A significant fraction of the research concerning atomic-scale characterization of C/M interfaces has been performed on model systems [1]. Such systems are prepared by a variety of methods including internal oxidation, diffusion bonding, or

\*Corresponding author. 2225 N. Campus Drive, Evanston, IL 60208-3108, USA. Tel.: 847-491-3575; fax: 847-467-2269.

E-mail address: j-sebastian@northwestern.edu (J.T. Sebastian).

molecular beam epitaxy [1]. The atomic-resolution techniques employed to study model interfaces have included one-dimensional atom-probe field-ion microscopy (1D-APFIM), high-resolution transmission electron microscopy (HREM), Z-contrast microscopy in a dedicated scanning transmission electron microscope (STEM), and electron energy-loss spectroscopy (EELS) in a dedicated STEM. In this paper, results from the application of three-dimensional APFIM (3DAP) [2–4] to the study of segregation of silver and antimony at MgO/Cu interfaces are presented.

The system  $\{222\}$  MgO/Cu(Ag) has been recently studied extensively [5,6]. The attractiveness of this particular system is attributable directly to the atomically clean and atomically sharp interfaces that can be produced by internal oxidation of high-purity Cu(Mg, Ag) alloys. The utilization of a Rhines pack to oxidize internally a Cu(Mg, Ag) alloy produces semi-coherent, octahedral-shaped MgO precipitates faceted on the close-packed  $\{222\}$  polar planes within a Cu matrix [7] (the lattice parameter misfit between MgO and Cu is 15.12%). Both experimental [7,8] and theoretical [9] results have shown that these precipitates are preferentially O-terminated. An EELS investigation of the  $\{222\}$  MgO/Cu interface has provided evidence for metal-induced gap states (MIGS) at this interface [8], which represents the first experimental observation of MIGS at any heterophase interface. In addition, one-dimensional APFIM and EELS investigations of this interface have permitted observation of Ag segregation on an atomic scale [6,10,11]. Silver segregation was measured quantitatively and the Gibbsian interfacial excess was determined directly [6,10,11]. Furthermore, the  $\{222\}$  MgO/Cu interface has been studied extensively by employing local density functional theory (LDFT) and molecular dynamics (MD) simulations [9,12–14].

## 2. Experimental procedure

### 2.1. Preparation of MgO/Cu(Ag) specimens

A Cu(Mg, Ag) alloy with the nominal composition Cu-2.5 at% Mg–0.8 at% Ag was prepared by

vacuum arc-melting. High-purity constituent elements (99.999 wt% Cu, 99.99 wt% Mg, and 99.999 wt% Ag) were used. Arc-melting produced a small ingot, which was subsequently swaged into a small rod and drawn into 200  $\mu\text{m}$  diameter wires. Recrystallization heat treatments were employed at various stages during the formation of the wires to facilitate cold working and to ensure that the final wires had a large grain size. The wires were then internally oxidized in a Rhines pack, consisting of a 1:1:1, by volume, mixture of Cu, Cu<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>, at 950°C for 2 h (the Al<sub>2</sub>O<sub>3</sub> is incorporated to prevent sintering of the Rhines pack). Internal oxidation under these conditions produces a distribution of octahedral-shaped MgO precipitates with a mean diameter of 20 nm and an average distance between precipitates of approximately 46 nm [5].

To enhance the segregation of Ag at the MgO/Cu interfaces, the internally oxidized wires were subjected to a segregation anneal. The latter was performed under an atmosphere of pure argon at 500°C for 72.5 h. Under these conditions, the minimum root-mean squared diffusion distance of Ag in Cu is approximately  $\sqrt{2Dt} = 1,520$  nm in one-dimension [15], where  $D$  is the diffusivity of the segregating species, Ag, and  $t$  is the annealing time. Therefore, since the average distance between precipitates is approximately 46 nm, it is likely that the segregating silver at the MgO/Cu interfaces is in global equilibrium with the silver in the copper matrix.

### 2.2. Preparation of MgO/Cu(Sb) specimens

A Cu(Mg) alloy with the composition Cu-2.46 at% Mg (as measured by direct current plasma emission spectroscopy by Luvak, Inc., Boylston, MA, USA) was prepared by vacuum arc-melting. The arc-melted ingot was swaged into a rod and drawn into 200  $\mu\text{m}$  diameter wires. The wires were recrystallized at 700°C for 17 h to increase the grain size, and were internally oxidized subsequently at 950°C for 2 h in a Rhines pack consisting of a 1:1:1, by volume, mixture of Cu, Cu<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> (the Al<sub>2</sub>O<sub>3</sub> is incorporated to prevent the sintering of the Rhines pack). As with the Cu(Mg, Ag) alloy, internal oxidation under

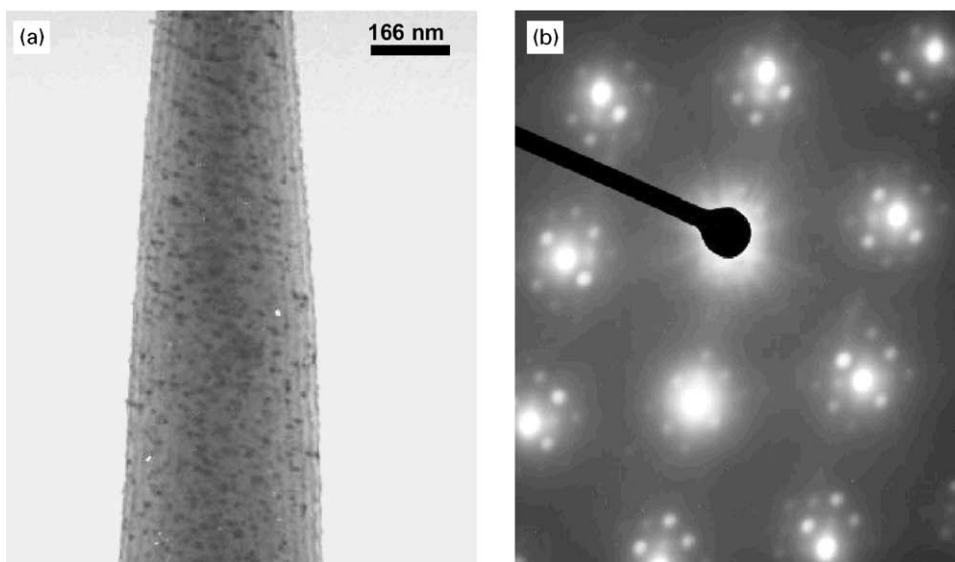


Fig. 1. (a) Bright field image of a MgO/Cu(Sb) specimen. The small, dark spots are precipitates; (b) selected area diffraction pattern of the same specimen in the  $\langle 110 \rangle$  orientation. The bright spots, originating from the copper matrix, are surrounded by satellite spots from the MgO precipitates.

these conditions produces a distribution of octahedral-shaped MgO precipitates with a mean diameter of 20 nm and an average distance between precipitates of approximately 46 nm [5] (see Fig. 1).

Antimony was introduced into the internally oxidized Cu(Mg) wires by means of a vapor treatment in a high-vacuum furnace. Antimony must be introduced by employing a vapor treatment after internal oxidation, because under the internal oxidation conditions used, the formation of antimony oxide also occurs. The experimental setup for the vapor treatment is shown in Fig. 2. The treatment was performed at a temperature of 700°C for 72 h. At this temperature, the solid-solubility of Sb in Cu is about 4 at% [16]. The high Sb concentration at the surfaces of the wires causes local melting. As a result, the wires were prevented from touching each other by placing them into small slits that had been cut into an Al<sub>2</sub>O<sub>3</sub> furnace boat. To further enhance the segregation of Sb at the MgO/Cu interfaces, a segregation anneal was performed subsequently at a temperature of 500°C for 24 h. Under these conditions, the minimum root-mean squared diffusion distance of Sb in Cu

is approximately  $\sqrt{2Dt} = 2,700$  nm in one-dimension [15]. Therefore, since the average distance between precipitates is approximately 46 nm, the segregating antimony at the MgO/Cu interfaces is most likely in global equilibrium with the antimony in the copper matrix.

### 2.3. 3DAP analyses of the specimens

For both specimen systems, wires for 3DAP analysis were prepared by electropolishing in a solution of 10 vol% Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in glacial acetic acid. The polishing voltage commenced at 20 V dc and was decreased stepwise to a final voltage of approximately 2 V dc.

For both specimen systems, 3DAP analyses were performed using a specimen temperature,  $T$ , of 45–50 K and a voltage pulse fraction,  $f$ , of 0.15 ( $f$  is the ratio of the pulse voltage to the steady-state dc voltage). Analyses on the MgO/Cu(Ag) system were performed using the energy-compensated optical position-sensitive atom probe (ECo-PoSAP) in the laboratory of Professor G.D.W. Smith at the University of Oxford, United Kingdom [3] (this research was performed as part of a

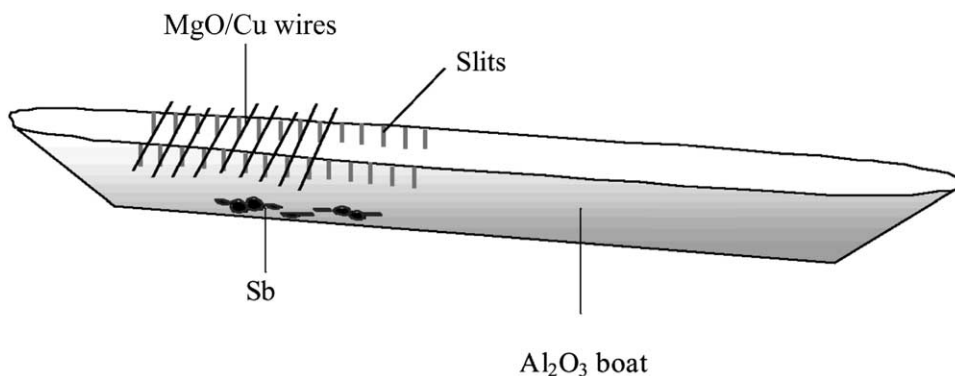


Fig. 2. Schematic diagram showing the setup used for the diffusion of Sb into the MgO/Cu specimens from the vapor phase.

contractual agreement between the Northwestern University and Kindbrisk Limited). Analyses on the MgO/Cu(Sb) system were performed using the 3DAP at the Northwestern University. The areal and length scales of the 3DAP atomic reconstructions were scaled as described in Refs. [17–19].

### 3. Results

#### 3.1. MgO/Cu(Ag)

Fig. 3 displays a 3D reconstruction of a MgO precipitate in a Cu(Ag) matrix. Magnesium atoms are in red, oxygen atoms are in green, and silver atoms are in blue. The copper atoms are shown as small green dots, allowing the precipitate to be distinguished clearly from the matrix. The overall dimensions of the reconstructed volume, which contains approximately 400,000 atoms, are 17 nm × 17 nm × 57.1 nm.

Fig. 4 shows another view of the same data set. In this figure, the matrix copper atoms are omitted for the sake of clarity. Overlaid on the reconstruction is an isoconcentration surface that delineates the surface of the MgO precipitate (and hence the MgO/Cu C/M interface). The isoconcentration surface is constructed such that all points *outside* the surface have a concentration level (of the specified species) *less than* a particular threshold value, whereas all points *inside* the surface have a concentration level *greater than* a particular

threshold value. In the case of Fig. 4, the isoconcentration surface represents a Mg concentration of 11 at%. This value defines the C/M interface close to the point of the steepest magnesium concentration gradient. At this point, the dependence of the location of the isoconcentration surface on the value of threshold concentration is weakest [20].

Fig. 5 exhibits a proxigram analysis [20] of the concentration of silver as a function of distance to the isoconcentration surface depicted in Fig. 4. Negative distances represent regions *outside* the isoconcentration surface, and positive distances represent regions *inside* the isoconcentration surface. The error bars represent the one-sigma error in the calculated concentration values.

#### 3.2. MgO/Cu(Sb)

Fig. 6 shows a 3D reconstruction of a MgO precipitate in a Cu(Sb) matrix. The MgO precipitate was encountered at the end of a 3DAP analysis. As a result, the precipitate appears only in the back corner of the reconstruction. Magnesium atoms are in red, oxygen atoms are in green, and antimony atoms are large and in blue. The matrix copper atoms are shown as small yellow dots, allowing the precipitate to be distinguished clearly from the matrix. The overall dimensions of the reconstructed volume, which contains approximately 60,000 atoms, are 11.7 nm × 11.5 nm × 13.8 nm. The segregation of the large, blue

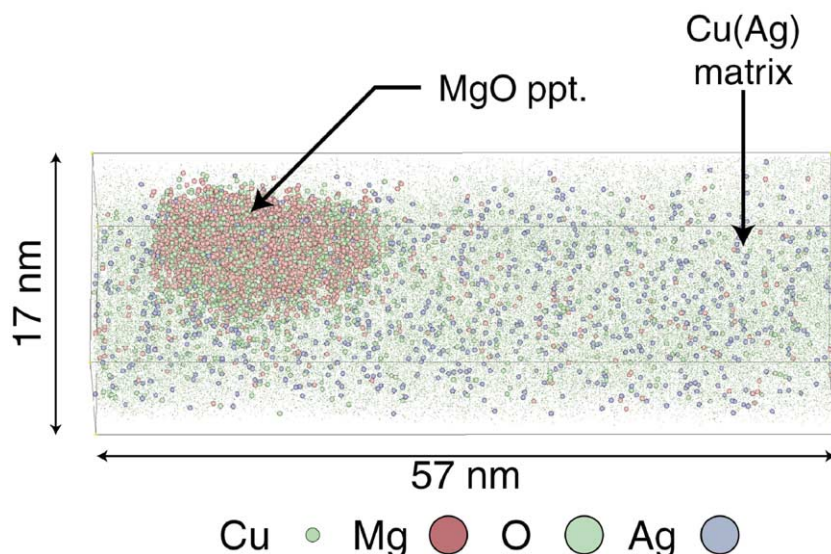


Fig. 3. 3DAP reconstruction of an internally oxidized Cu(Mg, Ag) alloy. Magnesium atoms are red, oxygen atoms are green, silver atoms are blue, and the matrix copper atoms are small green dots. The dimensions of the reconstruction are approximately  $17\text{ nm} \times 17\text{ nm} \times 57\text{ nm}$  and the number of atoms is approximately 400,000.

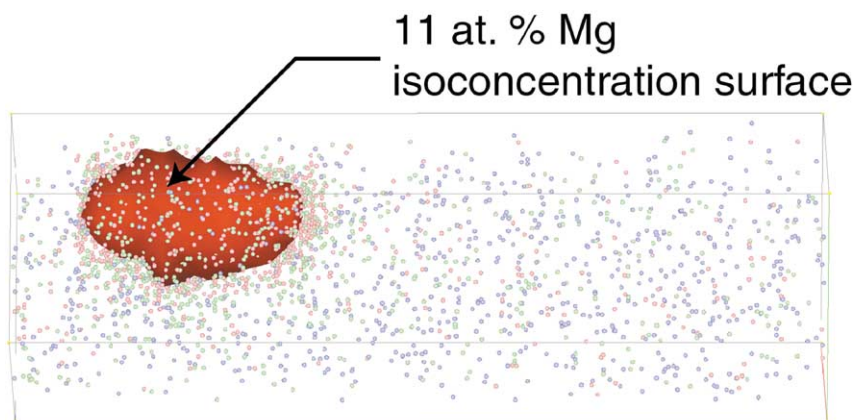


Fig. 4. A 11 at.% Mg isoconcentration surface overlaid on the data set shown in Fig. 3. The matrix copper atoms have been removed for the sake of clarity.

antimony atoms to the MgO/Cu precipitate/matrix interface is evident qualitatively in this figure.

Fig. 7 shows a proxigram analysis [20] of the concentration of antimony as a function of distance to an isoconcentration surface overlaid on the data set depicted in Fig. 6 (the isoconcentration surface is not explicitly shown in Fig. 6).

This isoconcentration surface was constructed at a magnesium threshold level of 30 at% (that is, at the point of steepest magnesium concentration gradient). Negative distances represent regions *outside* the isoconcentration surface, positive distances represent regions *inside* the isoconcentration surface. The error bars represent the one-sigma error in the calculated concentration values.

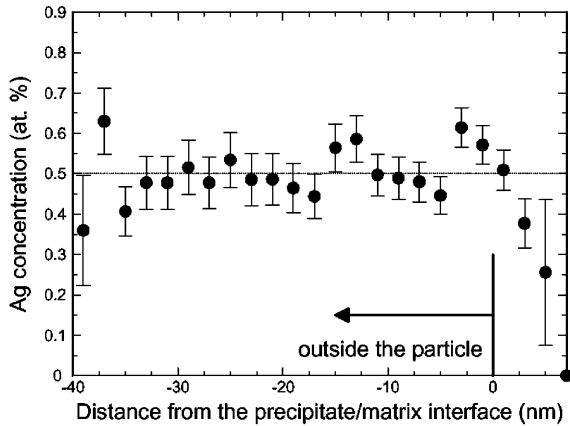


Fig. 5. Silver concentration (at.%) as a function of distance (nm) to the MgO/Cu isoconcentration surface depicted in Fig. 4. The bulk atomic concentration of Ag is approximately 0.5 at.%, as indicated in the figure. This figure is called a proximity histogram or proxigram for short [20].

#### 4. Discussion

The most significant information that can be extracted from the data presented in Figs. 3–7 is the Gibbsian interfacial excess,  $\Gamma_i$ , of the segregating species (that is, Ag or Sb). The quantity  $\Gamma_i$  is defined for a solute element  $i$  as

$$\Gamma_i = N_i^{\text{excess}}/A, \quad (1)$$

where  $N_i^{\text{excess}}$  is the excess number of atoms associated with an interface, and  $A$  is the effective interfacial area over which  $\Gamma_i$  is determined. The units of  $\Gamma_i$  are number per unit area. In Figs. 5 and 7, the proxigram analyses exhibit a peak in the concentration of Ag or Sb, respectively, near the location of the isoconcentration interface (where the abscissa equals zero). The area of this peak has units of “distance.” By multiplying this area with the theoretical atomic density (number of atoms per unit volume) of the specimen, a quantity with units of number of atoms per unit area is obtained. This number represents the Gibbsian interfacial excess of the segregating component at the interface [20]. The *theoretical* atomic density of the specimen, as opposed to the *actual* atomic density, of the reconstruction, is used since the difference in these densities (related to the detection efficiency of

the 3DAP) has already been taken into account when scaling the 3DAP data set.

The area of the peak in the proxigram in Fig. 5 (i.e., the area under the curve from approximately  $-5.0$  to  $2.5$  nm) is approximately equal to  $0.0038$  nm (note the units of “distance”). The theoretical atomic density of the copper matrix is approximately  $85 \text{ atoms nm}^{-3}$ . Therefore, the Gibbsian interfacial excess of Ag at the MgO/Cu interface, as determined from Fig. 5, is equal to

$$\begin{aligned} \Gamma_{\text{Ag}}^{\text{MgO/Cu}} &= (0.0038 \text{ nm})(85 \text{ atoms nm}^{-3}) \\ &= 0.32 \text{ nm}^{-2} \\ &= 0.32 \times 10^{14} \text{ cm}^{-2} \\ &= 3.2 \times 10^{17} \text{ m}^{-2} \text{ at } 500^\circ\text{C}. \end{aligned}$$

This value is for  $500^\circ\text{C}$  because the segregation annealing treatment of the specimen was performed at this temperature (see Section 2.1).

This value for  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  should be compared with the values reported for the same data set in Ref. [19]—between  $(2.33 \pm 0.88) \times 10^{18} \text{ m}^{-2}$  and  $(5.81 \pm 2.11) \times 10^{18} \text{ m}^{-2}$ —and the mean value reported for the same specimen system in Ref. [6]— $(4.0 \pm 1.9) \times 10^{18} \text{ m}^{-2}$ . The values reported in Refs. [6,19] are significantly higher than the value reported in the present paper. This apparent discrepancy can be understood in terms of the statistical techniques used to extract the value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  from the data sets. In Refs. [6,19], the integral profile method [21] of extracting  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  from the data was employed, whereas in the present paper, the proxigram method [20] is utilized. In using the integral profile method in Ref. [19], only the interfacial area corresponding to the intersection of an analysis cylinder with the front and back precipitate interfaces is sampled. In the proxigram method, the entire interfacial area of the precipitate is taken into account in the calculation of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$ . It is clear that in Ref. [19], the analysis cylinder intersected a region of locally high segregation, and a correspondingly higher value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  was extracted from the analysis. In the present paper, the value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  reported represents an average calculated from the entire precipitate interface, including regions of both locally



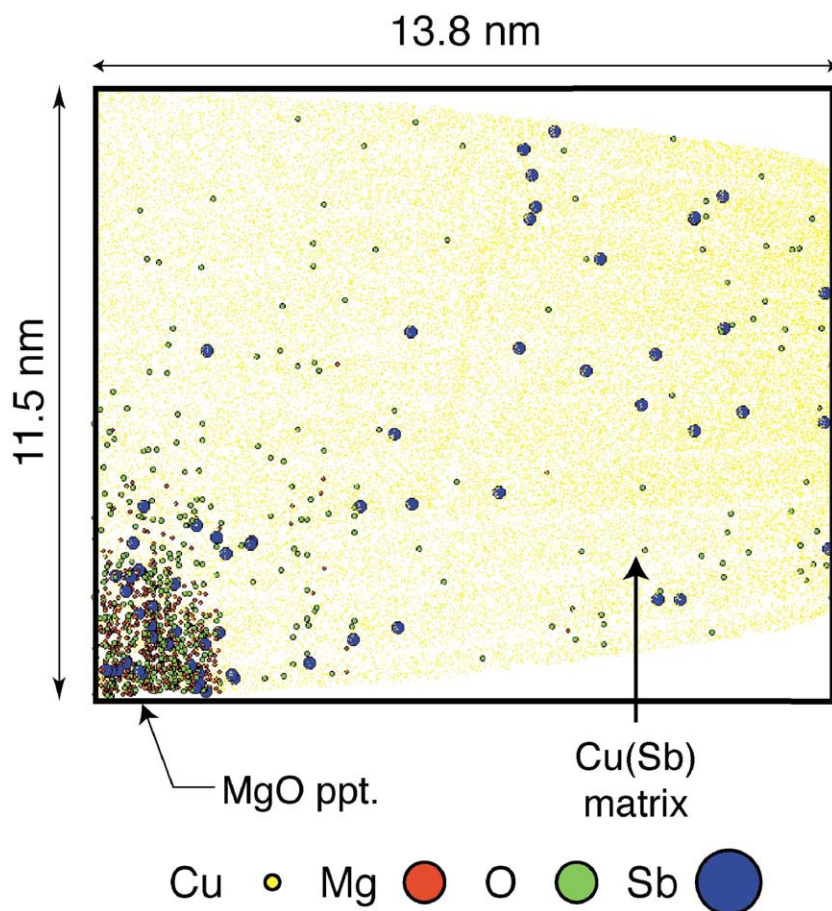


Fig. 6. 3DAP reconstruction of a MgO precipitate in a Cu(Sb) matrix. The MgO precipitate was encountered at the end of the 3DAP analysis. As a result, the precipitate appears only in the lower left-hand corner of the reconstruction. Magnesium atoms are in red, oxygen atoms are in green, and antimony atoms are large and in blue. The matrix copper atoms are shown as small yellow dots. The overall dimensions of the reconstruction are  $11.7 \text{ nm} \times 11.5 \text{ nm} \times 13.8 \text{ nm}$  and the number of atoms is approximately 60,000. The segregation of the large blue antimony atoms to the MgO/Cu precipitate/matrix interface is evident qualitatively from the figure.

high and locally low segregation. The two methods of extracting  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  are consistent and compatible. However, since the proxigram method examines the entire precipitate interface at once, it yields a number that is more representative of the average segregation behavior at the C/M interface as a whole. It is noted that the proxigram method is the only method capable of extracting the Gibbsian interfacial excess from non-planar interfacial structures.

The physical reason that Ag solute segregation is not uniform over the entire interfacial area of the C/M interface is connected with the mechan-

ism of a growing MgO precipitate losing its coherency with the Cu matrix. At very small sizes, the MgO precipitate is coherent with the Cu matrix, but as it grows, it can decrease its energy by nucleating an interfacial network of misfit dislocations and thereby becoming semi-coherent; note that the strain energy of a coherent precipitate is proportional to its volume. We have observed, employing dedicated STEM observations, an average interdislocation spacing of  $1.45 \pm 0.19 \text{ nm}$  at some  $\{222\} \text{MgO/Cu(Ag)}$  interfaces, which is in good agreement with the



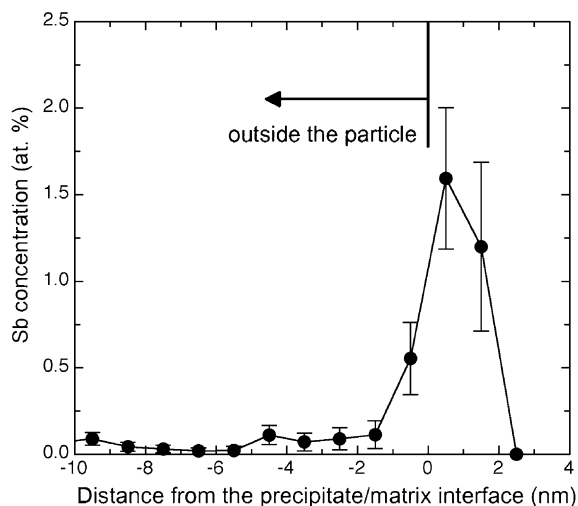


Fig. 7. Antimony concentration (at.%) as a function of distance to the surface of the MgO/Cu precipitate depicted in Fig. 6. A 30 at% Mg isoconcentration surface is used to delineate the MgO/Cu interface. The bulk atomic concentration of Sb is approximately 0.05 at%. This figure is called a proximity histogram or “proxigram” for short [20].

theoretical value [5]. In addition, we have used Z-contrast microscopy, in a dedicated STEM, to detect, qualitatively, the Ag segregation at  $\{222\}$ MgO/Cu(Ag) interfaces and have observed that not all interfaces have silver on them and also that the Ag is not always uniformly distributed around MgO precipitates [6]; this is because the entire interface does not have its full complement of misfit dislocations, which reflects an interfacial dislocation nucleation problem. These observations explain why the value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  is less when we measure it by the proxigram method as opposed to the integral profile method, which only samples a fraction of the interfacial area of the MgO/Cu(Ag) interfaces.

The proxigram method of extracting the Gibbsian interfacial excess has its sources of error in several different effects. First, and primary, is the uncertainty in the area of the peak in the proxigram itself (see Figs. 5 and 7). Other secondary sources of error include uncertainty in the threshold level of the isoconcentration surface used to construct the proxigram, field-evaporation effects in the vicinity of the precipitate/matrix

interface, and uncertainty in the atomic density of the reconstruction in the vicinity of the precipitate/matrix interface. These latter three sources of error, however, are thought to be insignificant relative to the primary source of error—the uncertainty in the area of the peak in the proxigram. Using the  $+\sigma$  error bars to calculate the area of the peak in the proxigram in Fig. 5 yields a value of 0.0062 nm. Using the data points themselves, a value of 0.0038 nm is obtained (as above). Using the  $-\sigma$  error bars to calculate the area of the peak in the proxigram in Fig. 5 yields a value of 0.0015 nm. Therefore, an estimate of the area of the peak in this proxigram, including error, is  $0.0038 \pm 0.0024$  nm. The corresponding value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$ , including error, is

$$\begin{aligned}\Gamma_{\text{Ag}}^{\text{MgO/Cu}} &= (0.0038 \pm 0.0024 \text{ nm})(85 \text{ atoms nm}^{-3}) \\ &= 0.32 \pm 0.20 \text{ nm}^{-2} \\ &= (0.32 \pm 0.20) \times 10^{14} \text{ cm}^{-2} \\ &= (3.2 \pm 2.0) \times 10^{17} \text{ m}^{-2} \text{ at } 500^\circ\text{C}.\end{aligned}$$

This value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$ , with error, is now compared with the values reported in Refs. [6,19]. Considering error bars, an upper threshold for the value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  reported in the present paper is  $5.2 \times 10^{17} \text{ m}^{-2}$  at  $500^\circ\text{C}$ . Also considering error bars, the lowest value for  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  reported in Ref. [19] is  $1.45 \times 10^{18} \text{ m}^{-2}$  at  $500^\circ\text{C}$ . The smallest experimental value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  reported in Ref. [6] is  $1.15 \times 10^{18} \text{ m}^{-2}$  at  $500^\circ\text{C}$ . It can be seen that the actual statistical discrepancy between the value of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  reported in the present paper and the values reported in Refs. [6,19] is less than a factor of three.

Using the  $+\sigma$  error bars to calculate the area of the peak in the proxigram in Fig. 7 yields a value of 0.045 nm. Employing the data points themselves yields a value of 0.034 nm. Utilizing the  $-\sigma$  error bars to calculate the area of the peak yields a value of 0.023 nm. Therefore, an estimate of the area of the peak in this proxigram, including error, is  $0.034 \pm 0.011$  nm. The theoretical atomic density of the copper matrix is approximately 85 atoms  $\text{nm}^{-3}$ . Hence, the Gibbsian interfacial excess

of Sb at the MgO/Cu interface, as determined from Fig. 7, is equal to

$$\begin{aligned} \Gamma_{\text{Sb}}^{\text{MgO/Cu}} &= (0.034 \pm 0.011 \text{ nm})(85 \text{ atoms nm}^{-3}) \\ &= 2.9 \pm 0.9 \text{ nm}^{-2} \\ &= (2.9 \pm 0.9) \times 10^{14} \text{ cm}^{-2} \\ &= (2.9 \pm 0.9) \times 10^{18} \text{ m}^{-2} \text{ at } 500^\circ\text{C}. \end{aligned}$$

This value is for 500°C because the segregation annealing treatment of the specimen was performed at this temperature (see Section 2.2). The value of  $\Gamma_{\text{Sb}}^{\text{MgO/Cu}}$  is more precise than that of  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  (that is, the relative error is much less) due to the fact that the peak in the proxigram in Fig. 7 is substantially more distinct than the peak in the proxigram in Fig. 5.

A note on the statistical significance of the values of Gibbsian interfacial excess presented above. It is true that the values of  $\Gamma_{\text{Sb}}^{\text{MgO/Cu}}$  and  $\Gamma_{\text{Ag}}^{\text{MgO/Cu}}$  presented are both extracted from the analyses of single precipitate/matrix interfaces. In this respect, their values may not be fully representative of the overall precipitate population. However, employing the proxigram method allows a large total interfacial area to be sampled. For example, if the precipitate in Fig. 4 is treated as a sphere of radius 5 nm (an approximation), then the total interfacial area sampled is approximately 300 nm<sup>2</sup>. Similarly, if the precipitate in Fig. 6 is treated as one-eighth of a sphere of radius 2.5 nm (again, an approximation), then the total interfacial area analyzed is approximately 10 nm<sup>2</sup>. These values for the area should be compared to the interfacial areas sampled in Ref. [19]. In this reference, analysis cylinders with diameters between 1 and 4 nm, with corresponding areas of approximately 0.8 and 13 nm<sup>2</sup>, respectively, were employed to sample the MgO/Cu(Ag) interface.

The precipitate in Fig. 6 appears in the back corner of the 3DAP reconstruction. At the end of the run corresponding to the reconstruction in Fig. 6, the MgO precipitate “popped out” of the specimen’s surface (indicated by a precipitous change in the steady-state dc voltage applied to the specimen, and an abrupt end to the detection of magnesium and oxygen ions). “Popping out”

creates an artifact back interface for the precipitate in the 3DAP reconstruction that appears flat. In order to prevent the inclusion of this back interface in the proxigram analysis of segregation, the data set was truncated slightly. The isoconcentration surface employed to obtain the proxigram information presented in Fig. 7 roughly resembles one-eighth of the surface of an ellipsoid positioned in the back corner of the 3DAP reconstruction.

As is evident from the above values, the Gibbsian interfacial excess of Sb at the MgO/Cu interface at 500°C is almost an order of magnitude higher than the Gibbsian interfacial excess of Ag at the MgO/Cu interface at the same annealing temperature. This is evident qualitatively by comparing Figs. 3 and 6: in Fig. 6, the segregation of Sb is readily apparent. The segregation of Ag in Fig. 3 is not evident until the proxigram analysis (Fig. 5) is performed.

In both specimens, the driving force for segregation may have its origin in two possible sources. First, the driving force for segregation can be related to the elastic strain energy associated with the volume change produced by the solute atom—the so-called  $p\Delta V$  effect. For this mechanism, the driving force is due to the release of strain energy in the matrix as a result of interfacial segregation. In terms of atomic radii, the volume difference between Cu and Ag atoms is approximately 44%, while the volume difference between Cu and Sb atoms is approximately 92% [22]. Therefore, the larger value of the Gibbsian interfacial excess of Sb at the MgO/Cu interface as compared to that of Ag can be understood in terms of this  $p\Delta V$  effect [23]. That is, the larger volume difference of the Sb atoms (relative to the copper matrix atoms) allows a greater release of strain energy at the interface. The second major explanation of segregation is related to the decrease of interfacial free energy as a result of segregation. The surface energy of a material scales with its absolute melting point to first order, and similarly, the grain boundary energy scales with the absolute melting point. The melting point of Cu, 1358 K, is significantly higher than that of Sb, 903.9 K. Therefore, Sb is expected to have a lower grain boundary energy than Ag, which melts at 1235 K, and the presence of Sb at a MgO/Cu

interface should result in a greater reduction of the MgO/Cu interfacial free energy than does the presence of Ag. The increased segregation level of Sb at MgO/Cu interfaces, as compared to that of Ag, may also be understood qualitatively in terms of this interfacial free energy effect. It is, however, noted that the  $p\Delta V$  effect is the dominant driving force for segregation in the systems investigated in the present paper.

The precipitates in the reconstructions in Figs. 3 and 6 appear somewhat diffuse and as a result, the precipitate/matrix interfaces appear somewhat “spread out”. Such effects are most likely artifacts of the field-evaporation process in the vicinity of a high-dielectric constant MgO precipitate [19]. The presence of such a precipitate at the surface alters the geometry of the local electric field, causing a divergence in ion trajectories [24]. A further complication arises due to the differences in the evaporation fields of the precipitate and the metal matrix, causing either a protrusion or a depression at the surface of the MgO precipitate. Both these factors result in a decrease in the local spatial resolution of the 3DAP, causing the precipitates to appear diffuse and the precipitate/matrix interfaces to appear “spread out”.

The “spreading out” of the interface does not, to first order, result in a change in the location of the interface within the 3DAP reconstruction. For this reason, the decrease in the local resolution of the 3DAP in the vicinity of C/M interfaces should not affect greatly the value of the Gibbsian interfacial excess,  $\Gamma_i$ , extracted with the proxigram method. The “spreading out” of the interface causes the segregation peak in the proxigram to have a greater width and a reduced height as compared to the proxigram analysis of an interface that is less “spread out”. To first order, the *area* of the peak, and the value of  $\Gamma_i$  extracted, does not change. In extracting a value of  $\Gamma_i$ , the proxigram method counts the number of segregating atoms in the vicinity of an interface, and divided it by the area of that interface (see Eq. (1)). Calculated in this way,  $\Gamma_i$  should not be affected (to first order) by a “spreading out” of the interfacial profile due to field-evaporation complications.

Finally, a note on the 3DAP experimental parameters employed. A specimen temperature of

45–50 K and a pulse fraction of 15% were employed for both analyses. A previous systematic study of the effects of atom-probe experimental parameters on the 1DAP analysis of MgO/Cu C/M systems determined that the values employed in the present study yielded the best results, with minimum complications due to preferential evaporation effects [25]. As described in Ref. [19], the precipitate depicted in Figs. 3 and 4 had an apparent copper concentration of approximately 50%. This high apparent concentration can be understood in terms of a combination of field-evaporation complications (as discussed above and in Ref. [19]) and preferential evaporation effects. It should, however, be noted that an incorrect value for the concentration of a precipitate does *not* affect the position of the precipitate/matrix interface, nor does it affect the value of the Gibbsian interfacial excess of a segregating solute species as determined by the proxigram method.

## 5. Conclusions

1. The results presented in this paper, along with results presented in Refs. [19,26], represent the first analyses of ceramic/metal interfaces by 3DAP microscopy. They also represent the first application of the proxigram method [20] for the direct determination of the Gibbsian interfacial excess of a segregating component at irregularly shaped internal heterophase interfaces.
2. The advantages of using the proxigram method to extract values of the Gibbsian interfacial excess of solute, as compared to the integral profile method, are explained.
3. The Gibbsian interfacial excess of Sb at the MgO/Cu(Sb) interface at 500°C is  $(2.9 \pm 0.9) \times 10^{18} \text{ m}^{-2}$ , while the Gibbsian interfacial excess of Ag at the MgO/Cu(Ag) interface at 500°C is  $(3.2 \pm 2.0) \times 10^{17} \text{ m}^{-2}$ ; both were determined by the proxigram method. The former value is almost an order of magnitude higher than the latter. This large difference in the Gibbsian

interfacial excesses is apparent qualitatively from the 3DAP reconstructions.

4. The larger value of the Gibbsian interfacial excess of Sb at the MgO/Cu interface as compared to that of Ag can be understood in terms of the so-called  $p\Delta V$  effect. The volume difference between Cu and Ag atoms is approximately 44%, while the volume difference between Cu and Sb atoms is approximately 92%. Hence, Sb experiences a larger driving force for interfacial segregation, than does Ag.
5. The magnesia precipitates appear somewhat “diffused” in the 3DAP reconstructions. This effect is understood in terms of complications arising during the field-evaporation of a high-dielectric constant MgO precipitate from within the copper metal matrix. Such complications result in a decrease in the local resolution of the 3DAP. These complications, however, do not affect, to first order, the value of the Gibbsian interfacial excess of solute as extracted by the proxigram method. The 3DAP retains its ability to obtain heterophase interfacial chemical information on a subnanoscale level, even when analyzing complicated systems such as ceramic/metal interfaces.

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